NICOTINE SULFATE FROM *NICOTIANA RUSTICA*

When this work was initiated, consumption of nicotine as an ingredient of standard insecticides was steadily expanding. The supply of raw material, however, was limited by the supply of tobacco factory by-products. To ensure ample supplies fo nicotine, experiments on production of nicotine from *Nicotiana rustica* were undertaken. A new process for recovery of nicotine from *Nicotiana rustica* was developed. It consists in expressing the juice, which contains most of the nicotine, liming, clarifying, recovering the nicotine from the juice by liquid-liquid extraction with kerosene in a packed column, and finally contacting the kerosene extract with sulfuric acid to produce nicotine sulfate of commercial strength (40% nicotine). Process variables were studied on a small pilot plant scale. The equipment used is described in detail.

EDWARD L. GRIFFIN, JR., G. W. MACPHERSON PHILLIPS, JOSEPH B. CLAFFEY, JOHN J. SKALAMERA, AND E. O. STROLLE

Eastern Regional Research Laboratory, Philadelphia 18, Pa.

THE process described in this paper presents a unique application of liquid-liquid extraction, unique because the desired constituent is extracted directly from a plant juice.

Nicotine is usually prepared from low grade tobacco and tobacco wastes, but these sources have not always been sufficient to meet the demands for nicotine insecticides. *Nicotiana rustica*, which can produce about twice as much nicotine as the commercial varieties of *N. tabacum* grown in the United States, has been suggested as an alternate source of supply.

Nicotine can be extracted from dried rustica by steam distillation in the same manner as from dried tobacco, but this requires drying the green plant for storage if the factory is to operate throughout the year; also, large amounts of steam are required for processing. The present investigation was carried out to study the feasibility of an alternate nicotine-recovery process, wherein juice expressed from the green rustica is limed, clarified, and extracted with kerosene, and the kerosene extract is reacted with sulfuric acid solution to produce a 40% nicotine solution as nicotine sulfate. The green plant would have to be pressed immediately after harvesting, but once limed, the juice can be stored indefinitely. The step of liquid-liquid extraction of the nicotine from rustica juice was studied in the most detail because it is the most novel feature of this process.

Process and Equipment

The flow sheet, Figure 1, shows the process steps and equipment used. Because the units listed are not of uniform capacity, they do not form an integrated pilot plant in which all units can be operated continuously.

To express the juice, the whole mature rustica plants were chopped on a rotary forage cutter and passed three to five times through a 10 × 14 inch sugar cane mill. Water equal to about 60% of the wet weight of the pressed cake was added to it before the third and each subsequent pressing. In this manner about 93% of the nicotine can be pressed out by five pressings as a juice containing about 0.5% nicotine. A continuous rotary cone press of the Davenport type was equally suitable for pressing juice from green rustica, provided the plant was first disintegrated in a hammer mill. Engineering details of these operations will be discussed in a paper now in preparation (*2*). After being screened through a 200-mesh screen, the juice was mixed with 1.5% slaked lime and stored in steel drums at room temperature until used.

The clarification equipment consisted of a pair of 100-gallon stainless steel tanks with partial jackets and a 12-inch aluminum plate-and-frame filter press.

The equipment for extracting with kerosene and the equipment for contacting the extract with sulfuric acid were set up together as an integrated unit (Figures 2 and 3) but were not operated simultaneously because their optimum operating capacities were different. The liquid-liquid extraction column consisted of a 12-foot section of 4-inch black iron pipe, jacketed with a 6-inch black iron pipe, and packed with Raschig rings. At the top and bottom of the column were unpacked glass sight chambers 1 foot long by 4 inches inside diameter. Supply tanks and receivers were 54-gallon open steel drums coated with a paint resistant to acid and kerosene. The kerosene used had a boiling point range of 200° to 255° C. and a density of 0.8154. Clarified rustica juice and kerosene were pumped separately, each through a rotameter and a heater, to the top and bottom of the column, respectively. The extract and the stripped juice flowed by gravity through coolers to receivers. In the column, the juice was the continuous phase; the interphase level was maintained at the center of the upper sight glass by manually adjusting a control valve on the stripped juice outlet. All piping on this extraction unit was made of black iron. Hot water was recirculated to the jacket and heaters from a 54-gallon supply tank provided with a temperature controller which injects steam. The temperature of the heated kerosene and juice was controlled by adjusting the amount of hot water circulated to each heater. Water from these heaters was then circulated to the jacket along with sufficient cold water (manually controlled) to give the desired jacket temperature. The jacket inlet temperature was measured by a dial thermometer. The temperatures of the inlet liquid, the outlet liquids, the cooled extract and the hot water supply were measured by thermocouples and a recording potentiometer.

The acid-contacting section consisted of two stages in series, operated continuously with respect to extract but batchwise with respect to acid. All flow rates were controlled by needle valves and rotameters except the acid rate in the first stage; here a metering pump was used because the variable viscosity of the liquid would prevent accuracy in the rotameter reading. All parts were made of Monel metal except the separators; these were constructed of wood and coated with resistant varnish.

The separators were open boxes 24 inches long by 12 inches deep by 6 inches wide (inside dimensions), each divided into sec-

tions as shown in Figure 2. The juice entered behind a baffle 1 inch from the feed end and passed over the top or through holes in the bottom into an 18-inch long settling section, which holds about 5.4 gallons, including the acid. The kerosene then overflowed into a 2-inch holding chamber at the outlet end, from which it passed to the second-stage separator or to storage. A sight glass permitted ready observation of the level in both the settling and holding sections.

Fresh 22.5% sulfuric acid was placed in the second stage, and second-stage acid from a previous run was placed in the first stage. In each stage, the extract was thoroughly mixed with one fourth of its volume of acid by passing through a centrifugal pump; it was then allowed to separate, the extract passing through the separator and the acid being recycled until the nicotine concentration in the first stage was estimated to have reached its maximum level. At this point, each run was halted, and the feed, raffinate, and acid fractions were analyzed for nicotine content by the spectrophotometric method developed by Willits *et al.* (*3*).

In a production plant the nicotine sulfate fraction would then be neutralized with caustic soda to a pH of at least 6 to prevent excessive corrosion of steel containers used for shipping. On a continuous basis, it would be possible to feed acid and remove product continuously or periodically without shutting down the plant.

Clarification

The limed juice should be clarified before extraction with kerosene to prevent fouling of the column. After the limed juice has settled, 85 to 90% of the juice can be decanted off readily. Most of the nicotine remaining in the sludge can then be recovered by two successive rinsings with water equal to the volume of the sludge, the recovery being in proportion to the drawoffs obtained.

The most satisfactory clarification process consisted in decanting most of the juice from the residue, rinsing the sludge twice, heating the combined juice and rinse water to 200° F. for 30 minutes, filtering with about 0.2% diatomaceous filter aid (about 6 square feet of filter area required per 100 gallons of juice), heating with about 0.7% soda ash to 180° F. for 30 minutes and refiltering through about the same area. This process gave juice which remained clear for several hours at 160° F. in contact with kerosene.

If the sludge is not removed by decanting, the same process can still be used for clarification, but then the filter aid and first filter area requirements are increased five- to sixfold, and the sodium carbonate and second filter area requirements are doubled.

Filtration of the juice was facilitated by holding it at 200° F.; lower temperatures were less satisfactory and higher temperatures gave no advantage. This filtered juice without the recommended sodium carbonate treatment gave further precipitation, and during kerosene extraction in the column a precipitate collected at the liquid-liquid interface. Fouling of the packing was only slight, however, and if material accumulated at the interface is drawn off periodically, this extraction could presumably be carried on for a long period. A small column was operated in this manner for 100 hours continuously, and there was no indication that this run could not have been considerably prolonged. The additional treatment of the hot filtered juice with soda ash and refiltering gave a more stable juice. No filter aid was required. Virtually no precipitation in the column was observed after this treatment.

Liquid-Liquid Extraction

Flooding capacities of the 4-inch column were measured with kerosene-rustica juice and kerosene-water systems at 150° F. These data are plotted in conventional form in Figure 4. For a given solvent ratio, the limiting juice rate was 15 to 20% higher than the limiting water rate when 0.5-inch rings were used in the column; the limiting water rate was increased more than threefold when 1-inch rings were used.

Efficient extraction of nicotine from rustica juice with an immiscible solvent depends on a distribution between the two liquid favorable toward the solvent. Since this factor varies greatly with temperature, the equilibrium distributions of nicotine between water and kerosene were examined at various temperatures.

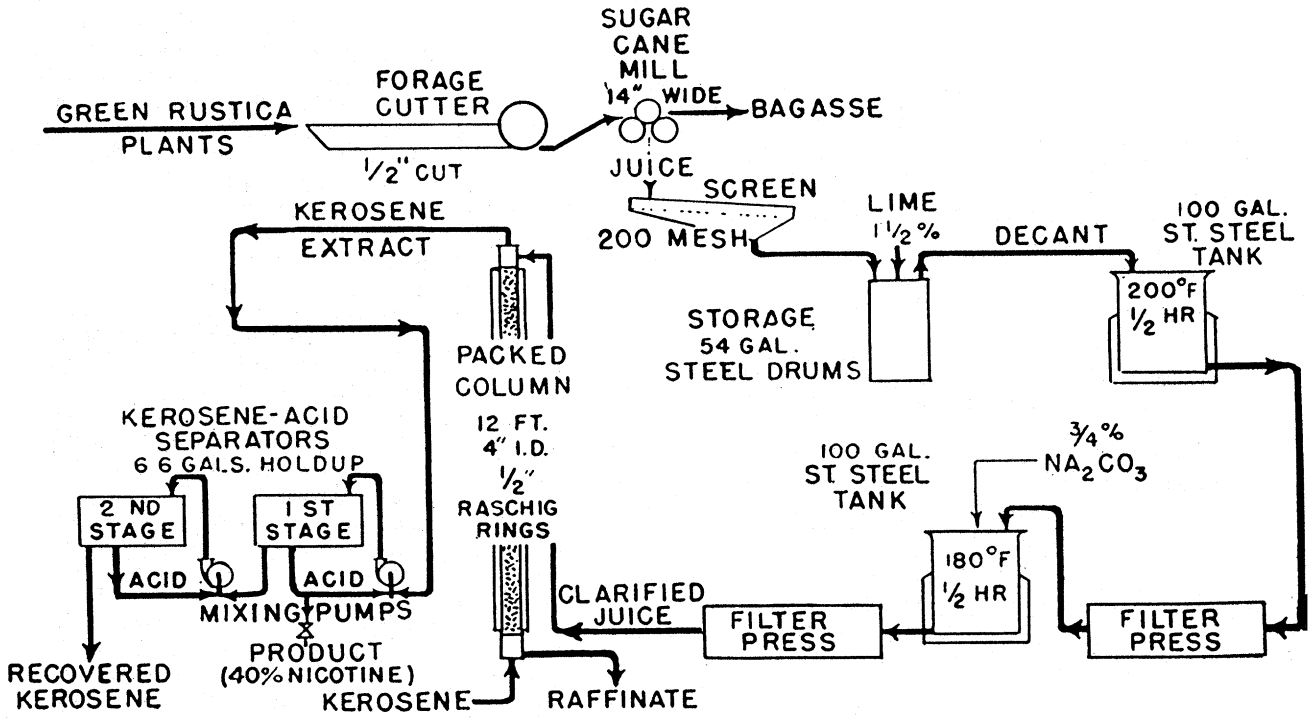

Figure 1. Production of Nicotine Sulfate from *Nicotiana rustica*

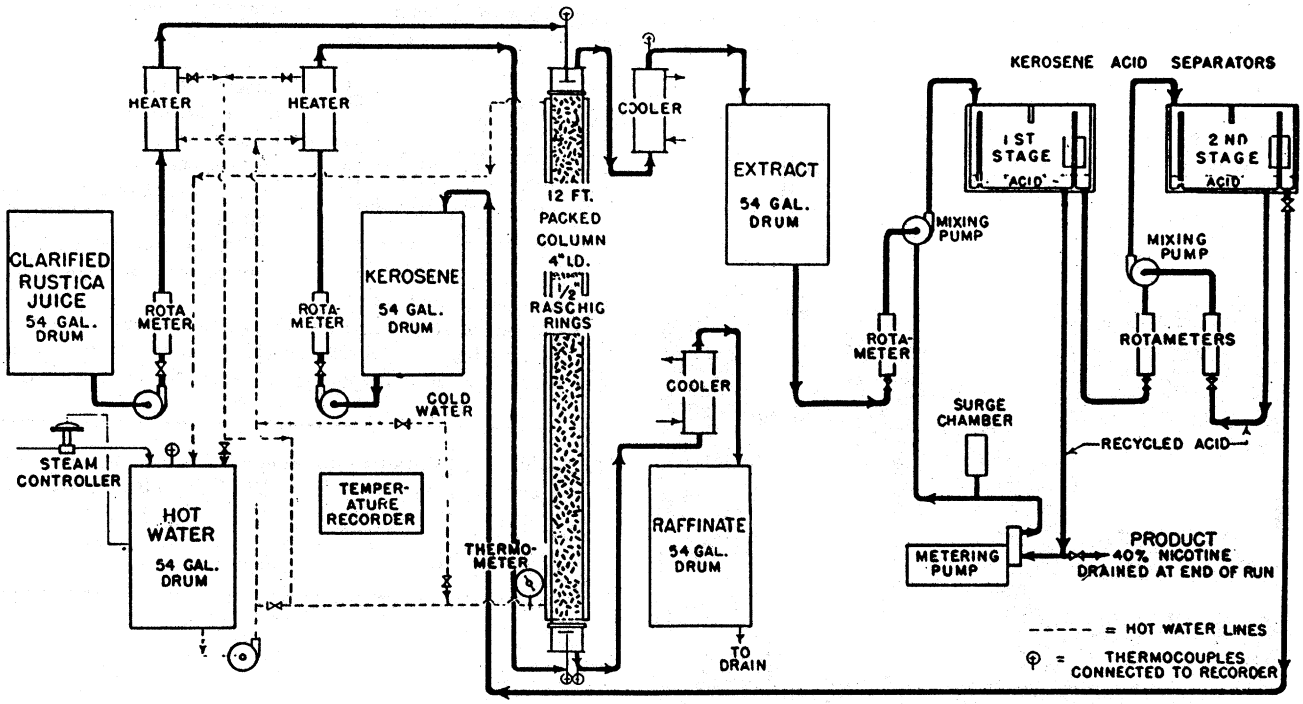

Figure 2. Details of Extraction and Acid-Contacting Sections

Water containing 0.5% nicotine was thoroughly admixed at each temperature with an equal volume of kerosene and each liquid was then titrated with sulfuric acid solution; methyl red was used as indicator. An equal volume of water was added to the kerosene samples prior to titration and thoroughly mixed with the kerosene during titration. The distribution coefficients thus determined form a straight-line graph on a logarithmic plot, as shown in Figure 5. Nicotine distribution coefficients for rustica juice and kerosene were determined by similarly mixing juice containing about 0.5% nicotine with kerosene and analyzing samples of both liquids. In several series of tests, each using samples of the same clarified rustica juice, the results above 120° F. were about the same as for water but were more spread out (Figure 5). Results at lower temperatures were generally erratic. The distribution coefficient shows continuous improvement with temperatures up to the highest temperature measured, 180° F.

Kerosene was used as the extracting solvent for all runs in the 4-inch column. The packed height was 12 feet in all cases. In each run, all conditions were held as nearly constant as possible until equilibrium conditions were obtained in the column. To facilitate obtaining equilibrium, the column was filled with water at the start, and some juice was fed before the kerosene feed was started. Samples of the extract were titrated with sulfuric acid every few minutes until a constant reading was obtained. The raffinate and extract were then directed to sample tanks until about 5 gallons of raffinate were collected. Samples of these equilibrium extracts and raffinates as well as the feed juice and solvent were then analyzed for nicotine to determine the extraction obtained.

The number of transfer units (N_{OR}) and the over-all height of one transfer unit (H.T.U.$_{OR}$) based on the raffinate phase are used as a measure of the extraction capacity of the column. Because only dilute nicotine solutions are involved and the entering solvent concentration is zero, transfer units are calculated by the following equation (*1*), in which subscript R, indicating the raffinate phase, is used in place of subscript W used in the reference.

$$N_{OR} = \frac{1}{1 - \frac{mL_R}{L_E}} \ln \left[\left(1 - \frac{mL_R}{L_E} \right) \frac{y_1}{y_2} + \frac{mL_R}{L_E} \right] \quad \text{and} \quad \text{H.T.U.}_{OR} = \frac{Z}{N_{OR}}$$

where m = distribution coefficient; $\frac{L_R}{L_E}$ = solvent ratio; y_1 = nicotine concentration in feed; y_2 = nicotine concentration in raffinate; and Z = packed height of column.

Preliminary tests of the column were made with a solution of 0.5% nicotine in water in place of the rustica juice. Data from these tests are listed in Table I. Over-all extractions of these solutions were consistently lower than extractions of rustica juice under the same conditions. For example, compare 2J, 8J, and 15J in Table II with 1W, 3W, and 12W, respectively, in Table I. Nevertheless, results of these tests show qualitatively that the extraction capacity of the column packed with either 1/2-inch or 1-inch rings improves with temperature at least up to 162° F., the highest temperature actually used. Where a solvent ratio of 1:2 was used at about 150° F. the H.T.U.$_{OR}$ with 1-inch packing was roughly one third higher than the H.T.U.$_{OR}$ for 1/2-inch packing extrapolated to the maximum capacity of each packing.

In all extractions of rustica juice (Table II) except one (15J), 1/2-inch packing was used. Effects of solvent ratio and feed rate on extraction capacity were determined in a series of runs at about 148° F., where the distribution coefficient is fairly good. Variation of over-all extraction of nicotine and H.T.U.$_{OR}$ with solvent ratio and feed rate are shown in Figures 6 and 7. Extraction increased and H.T.U.$_{OR}$ decreased as the feed rate and solvent ratio were increased. Values of H.T.U.$_{OR}$ for all solvent ratios examined approached a value of about 2.45 feet at their flood point. This means, therefore, that these columns are most efficient when operated at their maximum capacity and that under these conditions H.T.U.$_{OR}$ varies only slightly with the solvent ratio. For a given packing size, temperature, and solvent ratio, it should be possible to calculate fairly accurately the column heights required for the desired extraction. Table III shows calculated capacities and heights to give 98% extraction for a column at 148° F. and packed with 1/2-inch rings. As the solvent ratio is decreased, the required packed height increases about in proportion to the increased juice capacity, and at some point becomes inconvenient. A low solvent ratio is desirable, however, because the extract concentration is proportional to its reciprocal. High extract concentration in turn reduces the cost of the acid-contacting step by reducing the volume of extract to be handled.

Table I. Kerosene Extraction of Nicotine from Water in 12-Foot Packed Column

Run No.	1W	2W	3W	4W	5W	6W	7W	8W	9W	10W	11W	12W
Packing size (Raschig rings), inch	1/2	1/2	1/2	1/2	1	1	1	1	1	1	1	1
Water rate, gal./hour	10	25	25	25	90	90	25	25	25	25	25	25
Solvent rate, gal./hour	10	12.5	12.5	12.5	45	45	12.5	12.5	12.5	12.5	12.5	12.5
Solvent ratio	1:1	1:2	1:2	1:2	1:2	1:2	1:2	1:2	1:2	1:2	1:2	1:2
Av. extraction temp., ° F.	150	136	152	162	150	150	80	110	138	150	152	160
Extraction, %	96.6	80.3	85.4	88.6	76.8	76.7	24.1	42.7	58.2	63.0	66.1	68.8
N_{OR}	4.02	2.21	2.57	2.88	1.85	1.85	0.338	0.673	1.05	1.63	1.32	1.39
H.T.U.$_{OR}$, feet	2.98	5.43	4.66	4.16	6.50	6.50	35.4	17.9	11.4	7.40	9.17	8.66

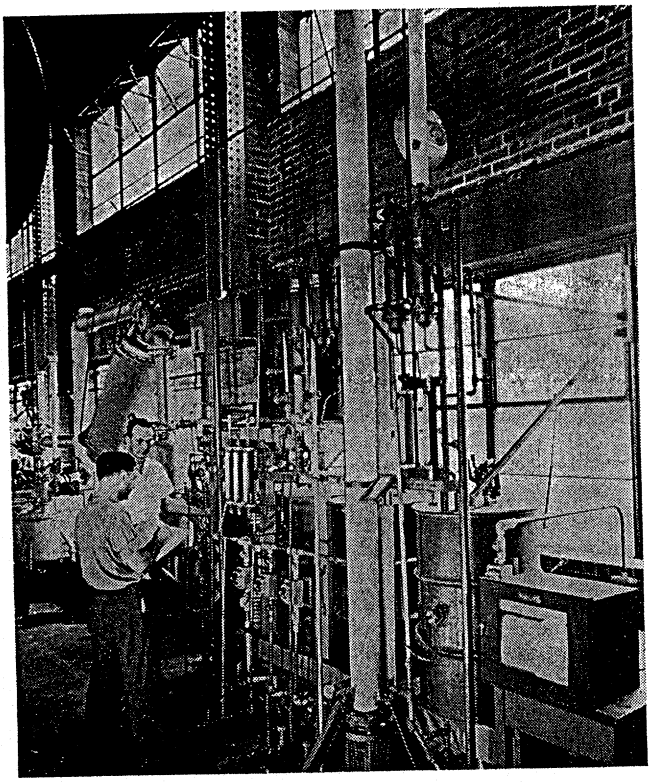

Figure 3. Extraction and Acid-Contacting Unit

Because the juice capacity rises as the solvent ratio is reduced, the volume of the column does not increase in proportion to the increased height of column required for the same extraction. The column volume required for 98% extraction at a unit juice rate passes through a minimum value at a solvent ratio slightly lower than 1:2.

Constant temperature was used in most of these runs to facilitate evaluation of the individual factors. Constant temperature, however, would not be important during a commercial production run as long as the minimum temperature is not too low. In general, hot juice would available from the clarification step, and the kerosene from storage would be near room temperature. In two runs using temperatures comparable to these (11J and 12J, Table II), extractions were about as good as extraction at a constant temperature of 149° F. Values of H.T.U.$_{OR}$ and average temperature cannot readily be determined for comparison.

A number of solvents, particularly chlorinated solvents, have considerably better distribution coefficients for extraction of nicotine from water even at room temperature than does kerosene at

Table III. Calculated Requirements of Column (Packed with 1/2-Inch Raschig Rings) That Will Give 98% Extraction

Solvent ratio	1:1	1:2	1:3
N_{OR}	4.7	5.9	8.1
Column height, feet	11.7	14.7	20.2
Maximum juice capacity, gal./hour/sq. foot	281	418	527

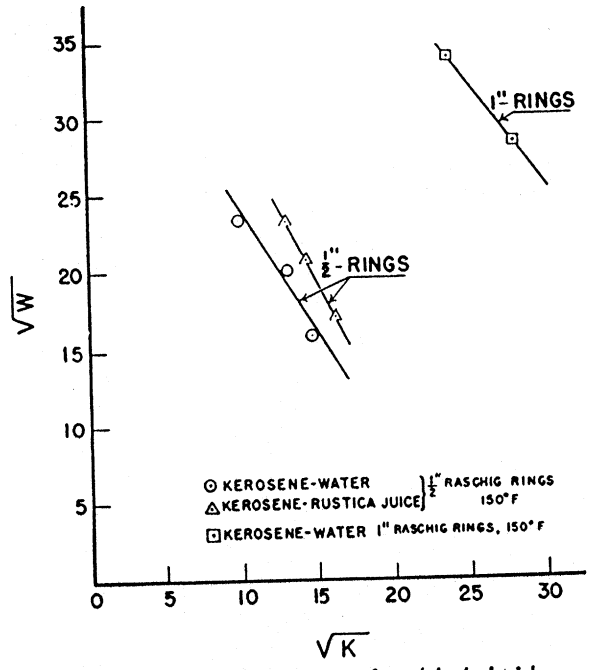

Figure 4. Flooding Curves for 4-Inch Inside Diameter Liquid-Liquid Extraction Column

W = Water rate, gal./hour/sq. ft.
K = Kerosene rate, gal./hour/sq. ft.

Table II. Kerosene Extraction of Rustica Juice in 12-Foot Packed Column

Run No.	1J	2J	3J	4J	5J	6J	7J	8J	9J	10J	11J	12J	15J	13J	14J
Packing size (Raschig rings), inch	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1	1/2	1/2
Solvent ratio	1:1	1:1	1:1	1:1	1:1	1:1	1:2	1:2	1:2	1:2	1:3	1:3	1:2	1:2	1:2
Juice rate, gal./hour	5	10	14	19	20	22	10	25	25	32	24	41	25	25	32
Solvent rate, gal./hour	5	10	14	19	20	22	5	12.5	12.5	16	8	13.7	12.5	12.5	16
Av. extraction temp., ° F.	146	146	146	148.5	148	150	147	149.5	149	149	149.5	149	148	[a]	[b]
Nicotine in feed, %	0.28	0.43	0.28	0.28	0.40	0.41	0.43	0.28	0.52	0.35	0.41	0.33	0.45	0.49	0.41
Nicotine in raffinate, %	0.007	0.009	0.005	0.007	0.007	0.007	0.03	0.015	0.03	0.016	0.067	0.03	0.10	0.03	0.01
Extraction, %	97.5	97.9	98.2	97.5	98.3	98.3	93.0	94.5	94.2	95.4	83.7	91.0	77.8	93.9	96.
Juice rate, gal./hour/sq. foot	57.3	114.5	160	218	229	252	114.5	286	286	367	275	470	286	286	367
N_{OR}	4.53	4.75	4.97	4.37	4.86	5.00	3.76	4.10	4.07	4.68	2.89	4.17	1.92	..	..
H.T.U.$_{OR}$, feet	2.66	2.53	2.42	2.75	2.47	2.40	3.19	2.93	2.94	2.62	4.15	2.88	6.28	..	..

[a] Temp. (° F.) to feed = 163°; solvent = 84°; raffinate = 140°; extract = 159°.
[b] Temp. (° F.) to feed = 168°; solvent = 95°; raffinate = 146°; extract = 164°.

50° F. One of these, orthodichlorobenzene, tried in a 1"/8-inch diameter extraction column, had definite possibilities but was not studied in detail. Its most obvious disadvantage is its relatively high cost. Other possible solvents are such compounds as tetrachloroethane, trichloroethane, dichlorodiethyl ether and dichlorobutanol.

Acid-Contacting Section

Nicotine was recovered from the kerosene extract by admixture of the extract with one fourth its volume of sulfuric acid followed by decantation in each of two successive steps. Because the general process of recovering nicotine from kerosene solutions by contact with sulfuric acid has been carried out commercially and is known to be operable, only sufficient work was done to prove the method operable on this extract also.

Sufficient admixture of extract and acid was readily obtained by pumping both liquids together through a small centrifugal pump driven only at sufficient speed to transfer the liquids at the required rate. Under these conditions, 100% extraction was obtained. After about 30 minutes settling in the continuous separators, the kerosene could be decanted at a rate of about 10 gallons per hour.

Excessive mixing action caused more emulsification and greatly increased the settling time required; consequently much larger separators would be required. Where the mixing pumps were run at high speed (3475 r.p.m.) and the flow rates were controlled by throttle valves, settling was not complete in many hours.

The wooden construction and the sealing compounds used for the separators were unsatisfactory as leaks developed during operation. (Lead lining would be more suitable.) In addition it was difficult to recover all the acid products from the separator lines and pumps. Hence, representative quantitative yields were not obtained for this step. Nevertheless, analysis of the products was significant in showing that the proposed two-stage process readily produces nicotine sulfate solution containing at least 40% nicotine, with insignificant loss of nicotine in the raffinate. Analyses of charges and products from a series of runs are shown in Table IV. All nicotine in the charge to the first stage in each case had been recovered from a previous run. Sulfuric acid of about 22.5% strength is required to give a product containing 40% nicotine, the usual commercial product. Proportionately higher concentrations were obtained when stronger acid was used.

In tests on nicotine solutions in kerosene, virtually complete extraction of the nicotine was obtained until the free acid content

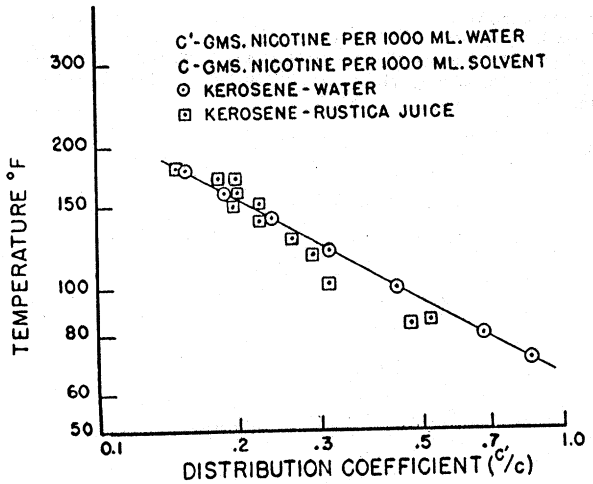

Figure 5. Nicotine Distribution Coefficients

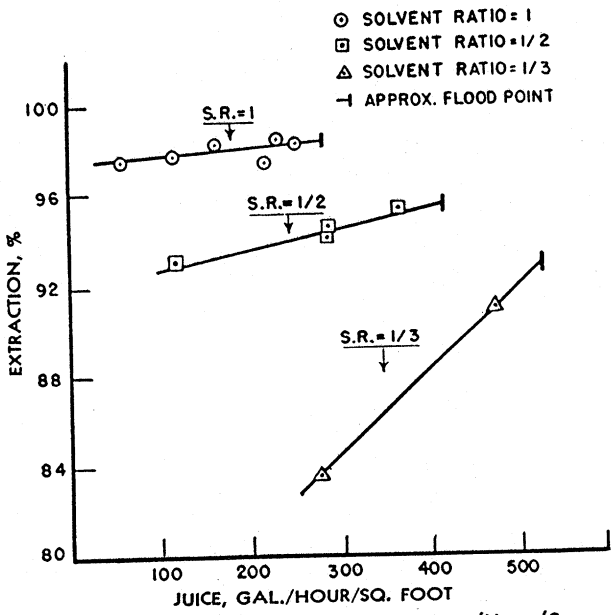

Figure 6. Per Cent Extraction vs. Gallons/Hour/Square Foot of Clarified Juice (about 148° F.)

Table IV. Acid Contacting of Kerosene Extracts

Run No.	1A	2A	3A	4A
Extract feed rate, gal./hour	10	10	10	10
Extract nicotine, %	0.53	0.81	0.98	0.97
Nicotine in recovered kerosene, %	Nil	Nil	Nil	Nil
Extraction, %	100	100	100	100
First stage				
Acid feed, lb.	2.4	3.2	3.2	2.24
H_2SO_4, %	25	9.07	8.94	16.9
Nicotine, %	0	25	25	10.8
Second stage				
Acid feed, lb.	2.4	2.4	2.4	2.4
H_2SO_4, %	25	24	23.5	22.8
First stage product				
Nicotine, %	43.9	41.8	41.5	40.8
H_2SO_4, %	0.12	..	..	..
pH	..	5.6	5.85	5.3
Second stage product				
Nicotine, %	8.64	17.2	10.8	26.2
H_2SO_4, %	..	14.4	16.9	8.5

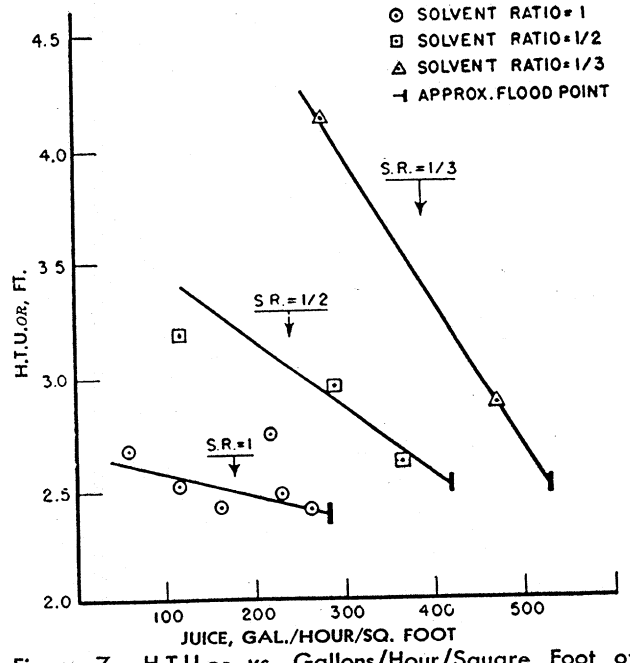

Figure 7. H.T.U.OR vs. Gallons/Hour/Square Foot of Clarified Rustica Juice (about 148° F.)

of the circulating acid fraction had dropped to about 5%. As the acid concentration decreased further by reaction with nicotine, the extraction dropped off somewhat, but was still about 67% when the product was nearly neutralized at a pH of 5.15. Most of the entering nicotine is therefore recovered in the first stage, at least until the acid is almost all neutralized. Hence, it should be practical to operate both stages continuously, feeding slightly more than the required acid to the second stage, drawing product from the first stage at a pH of 5.1 to 5.2, and neutralizing the unreacted acid.

Discussion

This work illustrates a new process for recovering nicotine from green plants containing substantial amounts of nicotine, which can be expressed effectively. The general process may also be applicable to the isolation of valuable constituents from other plants, provided that these constituents can be expressed in the liquor and a suitable immiscible solvent can be found.

All steps in the process operated satisfactorily. With the exception of expression of juice, all operations can be carried on throughout the year. The process eliminates the necessity of drying the plant material, and substitutes expression of juice for the steam distillation step conventionally employed with tobacco stems.

The over-all recovery of nicotine from the green plants can be relatively high, but in practice it will probably not be economical to recover more than about 85%. The largest part of this, about 8%, would be lost in the expression of juice. About 3% would be lost during clarification of the juice and possibly 2% each in the kerosene extraction and acid-contacting steps. Attaining higher yields in the pressing and clarification steps would result in increased dilution of the juice. Loss during extraction with kerosene is largely due to incomplete extraction of the juice and could be reduced by increasing the column height, if this is economical. Actual loss in the acid-contacting section would be primarily due to handling, because nicotine sulfate entrained through the settling chamber would be recovered ultimately by being recycled with the kerosene.

Acknowledgment

The authors are indebted to E. G. Beinhart for various suggestions and for supplying the *Nicotiana rustica* plants, and to C. O. Willits and J. A. Connelly for the analytical data.

Literature Cited

(1) Perry, J. H., "Chemical Engineers Handbook," 2nd ed., p. 1254, New York, McGraw-Hill Book Co., 1941.
(2) Phillips, G. W. M., *et al.*, "Cane Milling and Pressing of Nicotine from *Nicotiana rustica*," manuscript in preparation.
(3) Willits, C. O., Swain, M. L., Connelly, J. A., and Brice, B. A., *Anal. Chem.*, 22, 430 (1950).